Influence of strain on the properties of CeRuPO and CeOsPO Kondo systems

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Abstract

We investigated the influence of isotropic strain on the type of the magnetic ground-state and the Fermi surface for the structurally-equivalent CeRuPO and CeOsPO crystals with slightly different lattice parameters. The two systems exhibit different magnetic orderings at zero strain. According to the phase diagram of CeRuPO under pressure the difference might be due to the different Ce-Ce inter-atomic distances. We applied *ab-initio* calculations based on the density-functional theory and the generalized-gradient approximation with an additional Coulomb repulsion (GGA+U), which indeed reveal a significant impact of the strain and the effective U parameter on the magnetic ground state. However, it is demonstrated that the difference is more likely related to the details in the Fermi surface.

Keywords: magnetic ordering, strain influence, *ab-initio calculation*

1. Introduction

The existence of different phases under the same conditions in otherwise similar systems represents one of the important themes in contemporary condensed-matter physics[1]. Details in the electronic structure due to slightly different chemical compositions and, consequently, a subtle variation of the lattice parameters may lead to substantially different ground states. A classical example is the competition between the ferromagnetic (FM) and the antiferromag-

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netic (AFM) orderings, which is ascribed to different types of exchange coupling as well as to the fine tuning of the corresponding parameters, like the inter-atomic distances[2]. Although the heavy-fermion systems are more often regarded as antiferromagnetic, ferromagnetism in these materials is not so rare. Interestingly, most of the examples contain cerium as the source of magnetism[3, 4, 5, 6, 7, 8, 9]. A special consideration is required for CeRuPO, whose isostructural sister CeOsPO is antiferromagnetic[7]. Both, the ruthenium and osmium compounds crystallize in the tetragonal ZrCuSiAs-type structure (space group $P4/nmm$) consisting of alternating RuP_4 (OsP_4) and OCe_4-tetrahedra layers. The latter, which are magnetic, are well separated from each other. Therefore, a two-dimensional nature of the properties is expected. The unit cell of CeRuPO determined from the experimental lattice parameters $a = 4.028(1)$ Å and $c = 8.256(2)$ Å) is only very slightly smaller than the unit cell of CeOSPO with $a = 4.031(1)$ Å and $c = 8.286(3)$ Å. Nevertheless, the two materials exhibit different magnetic ground states. Recently, a pressure-dependent magnetic phase diagram for CeRuPO was determined[10]. The measured ^{31}P-NMR spectra were explained by a FM-to-AFM phase transition, which should occur when the sample is exposed to a pressure of about 0.7 GPa at nearly zero temperature. Above 2.97 GPa the measured signal indicated the existence of a paramagnetic ground state. Although the experiment covers just the unit-cell contraction due to the applied pressure, it is clear that the type of magnetic ordering can be determined by the strain in the material.

In order to better understand the influence of strain and to explore its importance with respect to the difference between the properties of CeRuPO and CeOsPO we carried out a theoretical investigation based on the density-functional theory (DFT). In fact, the corresponding band structures obtained from a DFT calculation for the non-strained states were already discussed[7]. The calculated total energies yielded the correct magnetic ground states. These band structures revealed only subtle differences, among which the slightly different oxygen hybridizations in both compounds were suggested as the most-likely reason for the different behavior of the two compounds.

2. Methods

We applied the Quantum Espresso[11] code and the generalized gradient approximation (GGA)[12] for the exchange-correlation potential. The electron-ion interactions were described with Troullier-Martins-type[13, 14] pseudopotentials. The strong correlations between the $4f$ Ce electrons were treated by means of the simplified rotational-invariant GGA+U scheme[15]. Since the calculated properties, to some extent, depend on the choice of the effective U parameter (see, for example, Ref. [16]), we performed the calculations for different values of $U = 0$ (pure GGA), 2, 4 and 6 eV. On the basis of convergency tests the plane-wave and the charge-density cut-off parameters were set to 1020 eV and 4080 eV, respectively, whereas a $4 \times 4 \times 2$ mesh of $\mathbf{k}$-points[17] was used for the Brillouin-zone integration[18]. The criterion for the self-consistency was the total-energy difference between the two subsequent iterations being less than 10^{-5} Ry. The theoretical equilibrium lattice parameters and the atomic positions were determined by means of minimizing the total energies and interatomic forces without taking into account spin the polarization and by setting the Coulomb repulsion to zero $U = 0$ eV. The resulting c/a ratio of 1.98 (1.97) for CeRuPo (CeOsPO) differs from the experimental value of 2.05 (2.06). The optimized structures were applied in the spin-polarized calculations for different types of magnetic ordering and values of U by varying the lattice parameter a, whereas the c/a value was fixed. A decrease in a has the same effect on the unit-cell volume as the application of an external pressure. In addition to the FM ordering we considered only the most simple AFM arrangement of the Ce magnetic moments pointing up and down at the two crystallographic sites within the unit cell.

3. Results and discussion

The total energies as a function of a are presented in Fig. 1. The calculated values are fitted with third-order polynomials $f^U(a) = f_3^U a^3 + f_2^U a^2 + f_1^U a + f_0^U$ and $g^U(a) = g_3^U a^3 + g_2^U a^2 + g_1^U a + g_0^U$ for the FM and AFM states, respectively. It

is clear that the theoretical equilibrium lattice parameter is almost independent of the type of magnetic ordering and grows very slightly with an increasing U. The experimental value is exceeded by 2.7%-3.5% in the case of the Ru and by 3.5%-4.2% in the case of the Os compound. Such a trend is in agreement with the GGA+U results for cerium oxides from Ref. [16]. The calculated values of the FM and AFM energies are very close to each other. Therefore, it is more illustrative to examine the differences $f^U(a) - g^U(a)$ presented in Fig. 2. A positive value implies the AFM, and a negative value implies the AFM ground state. The a dependence and the influence of the U value are pronounced. In the case of CeRuPO only $U = 4$ eV yields the proper FM ground state at the theoretical lattice parameter. For $U = 2$ eV the FM ground state exists at the experimental lattice parameter, whereas for $U = 6$ eV the FM state is energetically more favorable at larger values of a. At a strain of $\sim$ 8.4% the results of the calculation with $U = 4$ V predict a transition to the AFM state, which is in qualitative agreement with the experiment[10]. Krellner *et al.*[7] applied the LSDA+U method with $U = 6.4$ eV and found the correct FM ground state, but at the experimental lattice parameter. The system CeOsPO is less sensitive to the choice of U. Already a pure GGA calculation with $U = 0$ eV leads to the proper AFM ground state, which is also the case for $U = 2$ eV and $U = 4$ eV, whereas $U = 6$ eV predicts the FM ordering as being preferential for the whole range of a. Since there are no experimental results available for a strained CeOsPO it is hard to determine which of the U values is more appropriate. Both values $U = 2$ and 4 eV predict a transition to the FM state at high strains, which might be proved experimentally. In addition, for $U = 4$ eV the FM state prevails at a modest expansion of the unit cell. The calculated behavior of CeOsPO in principle supports the idea of the lattice-parameter mismatch as being the driving force for the difference in the magnetic ground states of the Ru and Os compounds. But the values of a at which the FM state becomes energetically favorable are much smaller than the equilibrium lattice parameter of CeRuPO. Furthermore, the calculations for CeRuPO do not exhibit the opposite behavior: within the whole considered

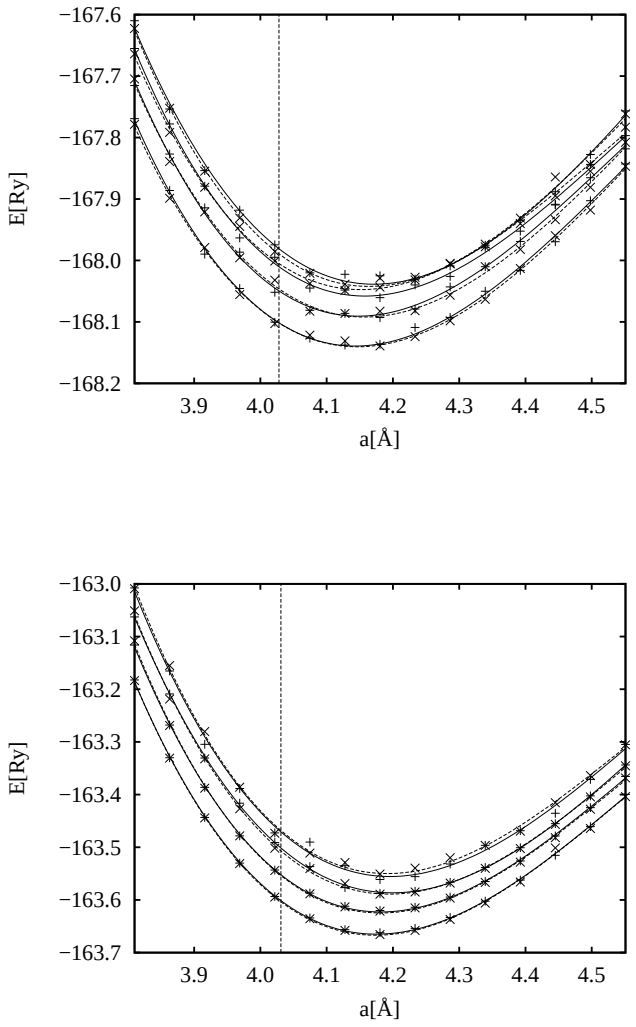

Figure 1: The calculated values of the total energies for the FM (+) and AFM (×) ordering in CeRuPO (top) and CeOsPO (bottom). The data are fitted with third-order polynomials $f^U(a)$ for FM (solid lines) and $g^U(a)$ for AFM ordering (dashed lines). The bunch of curves are for $U = 0, 2, 4$ and 6 eV from the bottom to the top. The vertical lines are positioned at the values of the experimental lattice parameters.

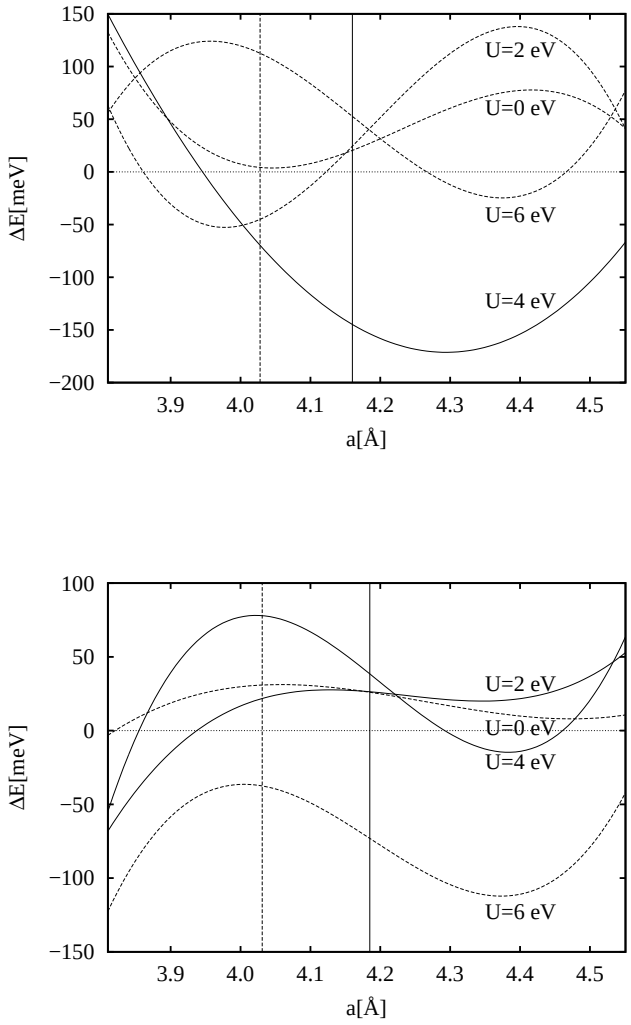

Figure 2: The difference in the total energy between the FM and the AFM states for CeRuPO (top) and CeOsPO (bottom) obtained from the 3rd-order-polynomial fits to the calculated values as a function of the lattice parameter a for different U values. The dashed vertical line is at the experimental and the solid vertical line is at the theoretical value of the lattice parameter. Positive values imply the AFM and negative values the FM ground state. Solid curves represent the theoretical predictions that reproduce the experimentally-observed behavior.

range of the positive strain the FM ordering remains in the ground state.

As demonstrated by Yamamoto and Si[19] the topology of the Fermi surface (FS) is one of the crucial factors for the type of magnetism in heavy-fermion systems. The calculated FS for $U = 4\,\mathrm{eV}$ and different values of a are presented in Fig. 3. At zero strain both, CeRuPO and CeOsPO FSs consist of three sheets per spin channel. As mentioned by Krellner *et al.*[7] the latter is represented by nearly perfect cylindrical tubes, typical for layered systems that exhibit two dimensionality[20]. In the case of the former, the inner-most tubes are deformed into pairs of mirror-symmetrical cones, which hints a non-negligible interaction between the RuP_4 and OCe_4-tetrahedra layers. This hypothesis is supported by the absence of cones in the FS for CeRuPO at large values of the lattice parameter $a = 8.6\,\mathrm{\AA}$. Since the c/a ratio is kept fixed the inter-layer distance grows too, and consequently the corresponding interaction gets weaker. The CeOsPO FS for the same value of the lattice parameter is even more cylindrical than in the case of the non-strained state, and all three sheets per spin are preserved although the inner-most tubes become very narrow. The outer-most tubes in the FS's of CeRuPO and CeOsPO for $a = 7.2\,\mathrm{\AA}$ are similarly distorted, indicating a more pronounced inter-layer interactions. The cones in the case of the Ru compound are even more significant than they are for the non-strained state. In the case of the Os compound the cylindrical tubes are almost non-distorted, although a pair of tiny cones appears for the down-spin channel as an additional fourth sheet.

4. Conclusion

On the basis of *ab-initio* calculations we determined the magnetic ground states for CeRuPO and CeOsPO isostructural systems as a function of the lattice parameter and the Coulomb-repulsion parameter U for the Ce $4f$ electrons. For $U = 4\,\mathrm{eV}$ all the available experimental results were fairly reproduced. The calculated Fermi surface of CeRuPO exhibits a less pronounced two-dimensional character than the one of CeOsPO due to a stronger interaction between the

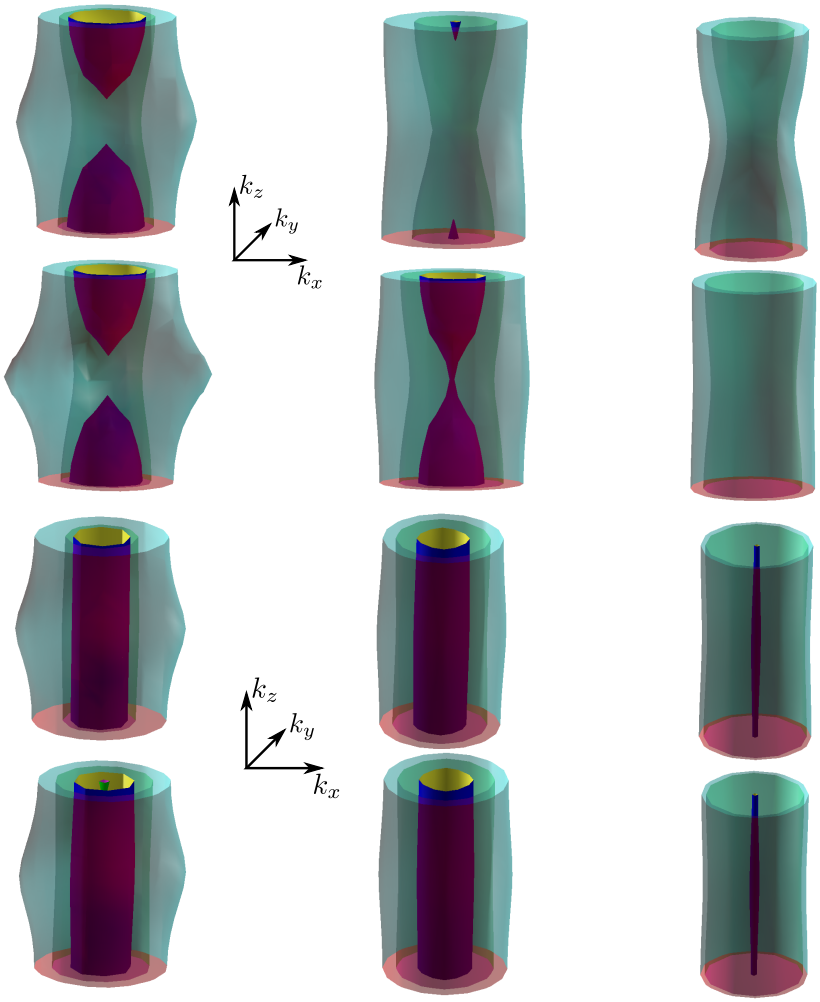

Figure 3: (Color online) The calculated Fermi surfaces for CeRuPO (top) and CeOsPo (bottom) by applying $U = 4\,\text{eV}$. In each figure the first row is for the spin up, and the second row is for the spin down. The left column is for $a = 7.2\,\text{Å}$, the middle column is for the theoretical equilibrium lattice parameter, and the right column is for $a = 8.6\,\text{Å}$.

layers within the crystal structure, which is probably the main reason for the different magnetic ground states of the two materials.

We call for a measurement of the pressure-dependent CeOsPO magnetic phase diagram.

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